

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 07-173452

(43)Date of publication of application : 11.07.1995

(51)Int.Cl.

C09K 3/00

A01N 25/00

A01N 25/26

B01J 13/04

C01B 33/18

C05G 3/00

C11B 9/00

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(22)Date of filing : 18.12.1993

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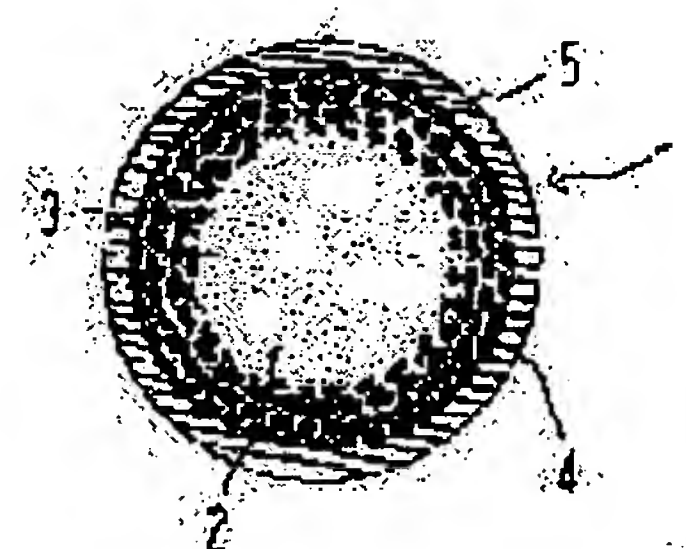
YOSHIKAWA HIDEYUKI

## (54) FINE POROUS INORGANIC PARTICLE

## (57)Abstract:

PURPOSE: To provide fine porous inorganic particles from which an enclosed functional substance is not easily eluted or evaporated even when the substance having a high water-solubility or volatility is incorporated in various base materials by enclosing the functional substance with the above particles, and coating the enclosing particles with a polymeric material.

CONSTITUTION: This particle 1 encloses the functional substance 3 of one or combination of two or more selected from among an antibacterial substance, a preventive against deposition of aquatic life, a perfume and an agricultural chemical, and is coated with polymeric material 5 (2: hollow part, and 4: micropore). The polymeric material 5 is one member or a combination of two or more selected from among proteins, polysaccharides, synthetic resin, latices and steroids. The polymeric material 5 may be water-soluble one. The fine inorganic porous particle is preferably a porous inorganic silica.



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CLAIMS

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[Claim(s)]

[Claim 1]Inorganic porosity particles characterized by covering with a polymer material while carrying out inclusion of what combined one sort chosen from an antibacterial substance, an underwater creature antibonding agent, perfume, and agricultural chemicals, or two sorts or more.

[Claim 2]The inorganic porosity particle according to claim 1 combining one sort chosen from protein, polysaccharide, a synthetic resin, latex, and steroid as said polymer material, or two sorts or more.

[Claim 3]The inorganic porosity particle according to claim 1 or 2, wherein said polymer material is water solubility.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention is applied to various fields and relates to the inorganic porosity particles which carry out inclusion of the functional material, such as an antibacterial substance, perfume, an underwater creature antibonding agent, and agricultural chemicals.

[0002]

[Description of the Prior Art]Conventionally, what carried out inclusion of the water-soluble and volatile high functional material to inorganic porosity particles, such as porous silica, is used for a ship bottom paint, an underwater creature antibonding agent, and other functional uses as high-performance material. Where inorganic porosity particles are warmed to a various substrate, scour this and it is crowded, or it is mixed to each solvent.

[0003]

[Problem(s) to be Solved by the Invention]Therefore, there was a problem. Namely, if inclusion of the water-soluble and volatile high functional material is carried out to inorganic porosity particles, and it scours to various substrates, such as a paint, ink, and cosmetics, and mixes [ it is crowded or ] to them, When content falls and the functional material by which inclusion must have been carried out actually uses it by elution, volatilization, etc. into a scour lump or a mixing process, when the amount of inclusion decreases, sometimes, there is a problem that effect becomes weak.

[0004]When carrying out inclusion of the underwater creature antibonding agent and using it for a ship bottom paint, by being immersed all over sea water, the underwater creature antibonding agent which carried out inclusion flowed easily, and the problem which is not maintained over a long time also had the underwater creature antisticking effect.

[0005]The purpose of this invention is what was going to improve inorganic porosity particles, and although it scours the high functional material of the water solubility by which inclusion was carried out to inorganic porosity particles, or volatility to a various substrate and is crowded, it tends to provide the inorganic porosity particles to which said functional material by which inclusion was carried out is eluted, and does not volatilize easily.

[0006]

[Means for Solving the Problem]The above-mentioned problem is solved by covering a polymer material to inorganic porosity particles. As a polymer material, and protein, polysaccharide, a synthetic resin, latex, What combined one sort chosen from steroid or two sorts or more is covered, water-soluble gelatin etc. are used as protein, and casein of insoluble in water nature, casein sodium, gluten, etc. are mentioned. A polysaccharide simple substance and its derivative can use as polysaccharide, and Gum arabic of water solubility [ it ], There are gellant gum, hydroxyethyl cellulose, carboxymethyl cellulose, hydroxypropylcellulose, psyllium seed gum, etc., and methyl cellulose of insoluble in water nature, ethyl cellulose, cellulose acetate, curdlan, etc. are mentioned. Poly vinyl alcohol water-soluble in a synthetic resin, a polyethylene glycol, A polypropylene glycol

etc. are used and an acrylic resin of insoluble in water nature, polymethylmethacrylate, polyvinyl acetate, polystyrene, Pori Sall John, etc. are possible, As latex, natural rubber latex, styrene butadiene copolymer latex, Polybutadiene latex, acrylonitrile butadiene copolymer latex, polyisoprene latex, polyvinyl acetate latex, polyvinyl chloride acetate copolymer latex, ethylene-vinylacetate copolymer latex, etc. are mentioned. Cholesterol of insoluble in water nature, etc. are mentioned as steroid. A polymer material may be water solubility.

[0007]As a method of coating said polymer material, spray dry, a granulation, vacuum drying, and freeze-drying are mentioned, and it is suitably used according to material.

[0008]As an inorganic compound in which what was excellent in a heatproof, water resistance, and corrosion resistance at inorganic porosity particles used here is desirable, and forms this inorganic porosity particle, It is usable in carbonate of alkaline-earth metals, silicate, phosphate, sulfate, a metallic oxide and metal hydroxide, other metallic silicates, or other metallic carbonate.

[0009]As carbonate of alkaline-earth metals, specifically Calcium carbonate, barium carbonate, carbonic acid -- a mug -- NEUMU etc. -- as the silicate of alkaline-earth metals -- a calcium silicate. barium silicate, a magnesium silicate, etc. -- moreover -- as the phosphate of alkaline-earth metals -- calcium phosphate, barium phosphorate, magnesium phosphate, etc. -- and as sulfate of alkaline-earth metals, calcium sulfate, barium sulfate, magnesium sulfate, etc. are mentioned again, respectively.

[0010]Furthermore, as a metallic oxide, silica, titanium oxide, iron oxide, cobalt oxide, a zinc oxide, nickel oxide, manganese oxide, an aluminum oxide, etc. are mentioned, and iron hydroxide, nickel hydroxide, aluminium hydroxide, calcium hydroxide, chromium hydroxide, etc. are mentioned as metal hydroxide, respectively.

[0011]And zinc silicate, aluminum silicate, etc. are mentioned as other metallic silicates, and zinc carbonate, basic copper carbonate, etc. are mentioned as other metallic carbonate, respectively. It is possible to use inorganic porous silica (trade name: God ball) already preferably marketed by these people.

[0012]A function is given by carrying out inclusion of what combined one sort chosen from an antibacterial substance, an underwater creature antibonding agent, agricultural chemicals, and perfume as functional material by which inclusion is carried out, or two sorts or more.

[0013]As an antibacterial substance by which inclusion is first carried out to such inorganic porosity particles, a thing with a germicidal action and a thing with bacteriostatic action are also contained. As a concrete antibacterial substance, 5-chloro-2-methyl-4-isothia \*\*\*\*\*- 3-one, 2-methyl-4-isothia \*\*\*\*\*- 3-one, 1,2-benziso thiazoline 3-one, 2-n-octyl-4-iso thiazoline 3-one, 2 -(4-thiazolyl)- Benzimidazole. Humulon (humulon), such as an antibiotic, the lupulone (lupulon), Allylsine, allylisothia NETO (allyl isotiocyanate), Chlorogenic acid, solanine, the tangeritin (tangeritin), Berberine, hinokitiol, iodine, an extract of a Japanese horseradish, forsythia extract, Rumpu roman extract, protamine, methylparaben, ethylparaben, Propylparaben, WANIRIN, thinner MIKKU aldehyde, p-hydroxy benzoate ester, d-limonene, ethyl alcohol, camphor, phenyloxide, p-dichlorobenzene, dimethyl fumarate, hiba oil, hiba arborvitae oil, Chamaecyparis taiwanensis oil, cassia oil, dill oil, lemon oil, citronella oil, clove oil, time oil, linalool, transformer PINOKARU Weor, p-isopropylcyclohexanol. Can FERE nick aldehyde, gamma-decalactone, g undecalactone, Formalin, hypochlorous acid NATORIMU, isopropanol, phenol, A benzalkonium chloride, chlorhexidine, a chloride alkyl diamide ethylglycine, A glutaraldehyde, chlorhexidine glyconate, thiabendazole, 2,4,5,6-tetrachloro isophthal nitril, a benzimidazole system compound, an organic iodine system compound, an organic nitrogen sulfur-systems compound, amino metal silver (product made from incorporated company Japanese ore), etc. are used.

[0014]As an underwater creature antibonding agent, 2-methylthio 4-t-butylamino 6-cyclobutylpropylamino S-triazine, 2,3,5,6-tetrachloro-4 (MACHIRU sulfonyl) pyridine, amino metal copper (product made from incorporated company Japanese ore), chloridation triphenyltin, acetic acid triphenyltin, triphenyltin hydroxide, tributyltin oxide, and TORIPURO pill tin chloride can be



mentioned.

[0015] Natural aromatic and synthetic perfume are used as perfume. As the natural aromatic, spearmint oil, peppermint oil, citronella oil, Eucalyptus oil, cascarilla oil, birch oil, cinnamon oil, What combined one sort chosen from clove oil, garlic oil, HAKKAOIRU, Marjoram oil, nutmeg oil, PAL MAROZA oil, SHISOOIRU, rose oil, savory oil, rosemary oil, lavender oil, etc. or two sorts or more is used. As synthetic perfume, amyl acetate, alpha-amylcinnamic aldehyde, Isoamyl salicylate, anisaldehyde, benzyl acetate, benzyl alcohol, What combined one sort chosen from borneol, l-carvone, menthol, citral, citronellal, citronellol, a coumarin, eugenol, a methyl salicylate, vanillin, a terpeneol, etc. or two sorts or more is used. A mixing-natural aromatic and synthetic perfume thing can also carry out inclusion.

[0016] An insecticide, a germicide, a nematocide, miticide, etc. are raised as agricultural chemicals. As a germicide, a dithiocarbamate agent, an organic sulfur (mancozeb etc.) system agent (captan etc.), Organophosphorus compounds (O,O-diisopropyl-S-benzylthio phosphate etc.), chlorinated organic compounds (pentachlorophenol etc.), an organoarsenic pesticide, and aliphatic series halogen (methyl ARUSENIKKUJI methylcarbamate etc.) agents (methyl bromide etc.) are mentioned.

[0017] As an insecticide, organo-phosphoric pesticides (dichlorvos etc.) and the Cava mate system insecticide (1-naphthyl N-methylcarbamate etc.), An organic halogen system insecticide and nicotine (DDT etc.) (nicotine etc.). Oil refinement (cineol, dill oil, Japanese mint oil, eucalyptus oil, TAPENTIN oil, etc.) of fluoroacetamide, pyrethroid (pyrethrine, allethrin, etc.), and vegetable origin, boric acid, etc. are used.

[0018] As miticide, Kelthane, prochlorol, a clo RUBEJI rate, chloropropylate, phenisobromolate, lavender oil, Melissa oil, peppermint oil, salvia oil, rosemary oil, etc. are used.

[0019] As a nematocide, there are a mixture of chloropicrin, 2,3-dichloropropane, and 1,3-dichloropropene, 1,2-dibromomethane, and a methylisocyanate, and a mixture of chloropicrin, 2,3-dichloropropane, and 1,3-dichloropropene, etc. are used preferably.

[0020]

[Function] While carrying out inclusion of what combined one sort chosen as inorganic porosity particles from an antibacterial substance, an underwater creature antibonding agent, perfume, and agricultural chemicals, or two sorts or more, the antibacterial substance, the underwater creature antibonding agent, the perfume, and the agricultural chemicals by which inclusion was carried out also on the conditions under underwater or an elevated temperature by covering with a polymer material -- elution -- it becomes difficult to volatilize. The functional material inclusion was carried out [ functional material ] to inorganic porosity particles by what combined one sort chosen from protein, polysaccharide, a synthetic resin, latex, and steroid as the polymer material or two sorts or more, and the water-soluble thing becomes eluting and being hard to volatilize. When using a water-soluble thing, the adjustment of time after being underwater immersed by adjusting the solubility until said inclusion thing flows out is attained, and it can realize sustained-release [ underwater ].

[0021]

[Example] Although the example of this invention is described below, referring to drawings, this invention is not restrained at all by this example.

[0022] Drawing 1 and drawing 2 are the structure table \*\*\*\*\* explanatory views which carried out inclusion of the underwater creature antibonding agent to the centrum, and covered porous silica (trade name: the God ball, the Suzuki oil and fat industry incorporated company make) with gelatin. This is in the state where the minute hole 4 is also filled up with the underwater creature antibonding agent 3 by which inclusion was carried out to the centrum 2 of said porous silica 1, and covers the gelatin 5 only to a peripheral part. Although not illustrated, inclusion of the underwater creature antibonding agent 3 is carried out only to the centrum 2 of said porous silica 1, and while being covered with the gelatin 5, there is also a thing in the state where the minute hole 4 was also filled up with the gelatin 5.

[0023] (Example 1) as Example 1 -- porous silica (trade name: -- the God ball.) The powder 20g of

seaweed-proofing agent 2,3,5,6-tetrachloro-4 (MACHIRU sulfonyl) pyridine (trade name: made in Densil-S-100 eye SHIAI Japan, Inc.) is melted in the solvent of methyl ethyl ketone as an underwater creature antibonding agent at the Suzuki oil and fat industry incorporated company make 200g. After making said porous silica impregnated, it was made to dry at about 50 °C for 2 hours. Thus, the obtained porous silica whole quantity containing a seaweed-proofing agent is distributed in 2 % of the weight of gelatin (trade name: made by gelatin 21 Nitta Gelatin, Inc.) solution 4000g. The porous silica which covered the gelatin containing an underwater creature antibonding agent which carried out coating treatment with gelatin under the conditions of 150 °C and 30000 revolutions per minute using the spray dry device (trade name: CL-8 the OHKAWARA KAKOHKI incorporated company make) was obtained.

[0024](Example 2) 200 g (trade name: made by God ball Suzuki oil and fat industry incorporated company) of porous silica which carried out inclusion of the volatile high jasmine perfume liquid 20g as Example 2, methylene chloride -- a solvent -- cholesterol: -- ethyl cellulose: -- it mixing by the ratio of polyethylene-glycol (molecular weight 20000) =1:2:1, distributing in the solution 300g 10% of the weight, and, The porous silica in which there is the scent of the jasmine which performed coating treatment using the vacuum freeze dryer (made in [ for 1 l. ] testing machine Toyo Research Institute, Inc.), and covered it by cholesterol, ethyl cellulose, and a polyethylene glycol was obtained.

[0025](Example 3) As Example 3, 10 g of porous silica which carried out inclusion of the rumput roman extract 5g as an antibacterial substance, Methanol was distributed in the solution 125g mixed [ 3 % of the weight of ethyl cellulose ] to the solvent, the continuation granulation dryer (made by OHKAWARA KAKOHKI incorporated company) performed granulation desiccation for 10 minutes, and the antibacterial porous silica covered by ethyl cellulose was obtained.

[0026](Comparative examples 1, 2, and 3) What is not performing coating treatment of Examples 1, 2, and 3 was obtained as the comparative examples 1, 2, and 3.

[0027](Test of Example 1 and the comparative example 1) Example 1 and the comparative example 1, Adjust so that it may become 5% of the weight in the acrylic resin system paints which dissolved in xylene, respectively, and the oiliness acrylic resin system paint containing a seaweed-proofing agent is produced, It actually applied to the ship's bottom, the seaweed-proofing test was done by sea immersion, and what observed adhesion of the alga with the naked eye weekly was shown in Table 1 over the period for eight weeks. It has prevented adhesion of the underwater creature of a ship's bottom over the long period of time as it was shown in Table 1, since it was coated by gelatin compared with the comparative example 1 and the rate of dissolution to the inside of sea water was slow Example 1.

[0028]

[Table 1]

船底塗料の防藻テスト結果

	1週目	2週目	3週目	4週目	5週目	6週目	7週目	8週目
実施例1	○	○	○	○	○	○	○	○
比較例1	○	○	×	×	×	×	×	×

○ : 藻の付着なし

× : 藻の付着有り

[0029](Test of Example 2 and the comparative example 2) Example 2 and the comparative example 2, It adjusted so that it might become 5% of the weight in acrylic emulsion system paints, respectively, and the perfume \*\*\*\*\* acrylic emulsion system paint of the jasmine was produced,

about 3 g was uniformly applied to plywood of 0.1 mm in thickness, and 5 cm around, and it dried at 20 \*\* for 5 hours. And days until the smell of the perfume is lost by an abuse test deed and organoleptics in the plywood in which the paint was applied with the homoiothermal constant humidity chamber whose temperature inside is 30 \*\* and whose humidity is 90% were shown in Table 2. Since coating treatment is carried out in this example, as it is shown in Table 2 compared with the comparative example 2, the duration in an abuse test is \*\*\*\*\* overwhelmingly.

[0030]

[Table 2]

ジャスミン香料の芳香性試験結果

	1日	2日	3日	4日	5日	6日	7日	8日	9日	10日	11日
実施例2	○	○	○	○	○	○	○	○	○	○	○
比較例2	○	○	○	○	×	×	×	×	×	×	×

○：芳香性有り

×：芳香性なし

[0031](Test of Example 3 and the comparative example 3) Example 3 and the comparative example 3, It adjusted so that it might become 5% of the weight in acrylic emulsion system paints, respectively, and the acrylic emulsion system paint containing an antimicrobial agent was produced, about 2 g was applied to the transparent-acrylic-resin board of 1 cm around at 0.1 mm in thickness, and it dried at the room temperature for 5 hours. It was neglected to the outdoors after that and evaluation of as opposed to [ over the period for eight weeks / weekly ] bacteria and true fungi for an antibacterial effect was carried out. as the bacteria used for the test -- punishment -- lath subtilis (Bacillus subtilis). Staphylococcus Aureus (Stapylococcus aureus), As Escherichia coli (Escherichia coli), Pseudomonas aeruginosa (Pseudomonas aeruginosa), and true fungi, Aspergillus Nigre (Aspergillus nigar), Aspergillus ORIZE (Aspergillus oryzae), Mucor RUKISHI (Mucor rouxi), Saccharomyces Selby Xie (Saccharomyces cerevisiae) has. An antibacterial test Glucose 1% (w/v) (made by best glucose Wako Pure Chem, Inc.), Yeast extract 2% (w/v) (made by Difco yeast extract Difco), To the GYP liquid medium which was adjusted the pH to 6.8 by peptone 1% (w/v) (made by Difco peptone Difco) of concentration, and it poured distributively 10 cc at a time in each test tube, and carried out sterilization treatment with autoclave. It adjusted so that bacteria and true fungi might become [ g ] in 100,000 pieces /, the acrylic resin plate which did the field test on this was put into in vitro, and bacteria are 37 \*\*, and true fungi were cultivated for three days with the thermostat at 28 \*\*, respectively, and performed growing conditions by macro-scopic observation. Since it was coated with ethyl cellulose and it was not emitted more than needed, its effect was long as Example 3 was shown in Table 3 compared with the comparative example 3.

[0032]

[Table 3]

抗菌テストの結果

供 試 菌		1週目	2週目	3週目	4週目	5週目	6週目	7週目
付着菌	実施例1	○	○	○	○	○	○	○
	比較例1	○	○	○	○	×	×	×
スチロコッカス フリウス	実施例1	○	○	○	○	○	○	○
	比較例1	○	○	×	×	×	×	×
大腸菌	実施例1	○	○	○	○	○	○	○
	比較例1	○	○	×	×	×	×	×
シュードモナス アエリナ	実施例1	○	○	○	○	○	○	○
	比較例1	○	○	×	×	×	×	×
アスベギルス ニガ	実施例1	○	○	○	○	○	○	○
	比較例1	○	○	○	○	×	×	×
アスベギルス オリゼ	実施例1	○	○	○	○	○	○	○
	比較例1	○	○	○	○	×	×	×
ムコール ルーシ	実施例1	○	○	○	○	○	○	○
	比較例1	○	○	○	×	×	×	×
サッカロマイセス セルビシエ	実施例1	○	○	○	○	○	○	○
	比較例1	○	○	×	×	×	×	×

○：抗菌力有り

×：抗菌力なし

[0033]The example which carried out coating treatment from the above result is shown from a comparative example by Tables 1, 2, and 3 where that effect is continuing over a long period of time expressed the result of each examination.

[0034]

[Effect of the Invention]By covering a polymer material, they can be prevented from the antibacterial substance, the underwater creature antibonding agent, the perfume, and the agricultural chemicals by which inclusion was carried out being eluted for a short time more than needed, or volatilizing, and an effect can be maintained over a long period of time. A good result is obtained by furthermore using what combined one sort chosen from protein, polysaccharide, a synthetic resin, latex, and steroid, or two sorts or more, and a water-soluble thing as a polymer material. When a water-soluble thing is used especially, adjustment of time after being underwater immersed by adjusting the solubility until said thing which carried out inclusion flows out can be attained, sustained-release [ underwater ] can be realized, and the effect outstanding as a ship bottom paint, or a seaweed-proofing agent and a lasting long aromatic can be demonstrated.

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TECHNICAL FIELD

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[Industrial Application]This invention is applied to various fields and relates to the inorganic porosity particles which carry out inclusion of the functional material, such as an antibacterial substance, perfume, an underwater creature antibonding agent, and agricultural chemicals.

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**PRIOR ART**

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[Description of the Prior Art]Conventionally, what carried out inclusion of the water-soluble and volatile high functional material to inorganic porosity particles, such as porous silica, is used for a ship bottom paint, an underwater creature antibonding agent, and other functional uses as high-performance material. Where inorganic porosity particles are warmed to a various substrate, scour this and it is crowded, or it is mixed to each solvent.

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EFFECT OF THE INVENTION

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[Effect of the Invention]By covering a polymer material, they can be prevented from the antibacterial substance, the underwater creature antibonding agent, the perfume, and the agricultural chemicals by which inclusion was carried out being eluted for a short time more than needed, or volatilizing, and an effect can be maintained over a long period of time. A good result is obtained by furthermore using what combined one sort chosen from protein, polysaccharide, a synthetic resin, latex, and steroid, or two sorts or more, and a water-soluble thing as a polymer material. When a water-soluble thing is used especially, adjustment of time after being underwater immersed by adjusting the solubility until said thing which carried out inclusion flows out can be attained, sustained-release [ underwater ] can be realized, and the effect outstanding as a ship bottom paint, or a seaweed-proofing agent and a lasting long aromatic can be demonstrated.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention]Therefore, there was a problem. Namely, if inclusion of the water-soluble and volatile high functional material is carried out to inorganic porosity particles, and it scours to various substrates, such as a paint, ink, and cosmetics, and mixes [ it is crowded or ] to them, When content falls and the functional material by which inclusion must have been carried out actually uses it by elution, volatilization, etc. into a scour lump or a mixing process, when the amount of inclusion decreases, sometimes, there is a problem that effect becomes weak.

[0004]When carrying out inclusion of the underwater creature antibonding agent and using it for a ship bottom paint, by being immersed all over sea water, the underwater creature antibonding agent which carried out inclusion flowed easily, and the problem which is not maintained over a long time also had the underwater creature antisticking effect.

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**MEANS**

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[0010]Furthermore, as a metallic oxide, silica, titanium oxide, iron oxide, cobalt oxide, a zinc oxide, nickel oxide, manganese oxide, an aluminum oxide, etc. are mentioned, and iron hydroxide, nickel hydroxide, aluminium hydroxide, calcium hydroxide, chromium hydroxide, etc. are mentioned as metal hydroxide, respectively.

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[0012]A function is given by carrying out inclusion of what combined one sort chosen from an antibacterial substance, an underwater creature antibonding agent, agricultural chemicals, and

perfume as functional material by which inclusion is carried out, or two sorts or more.

[0013]As an antibacterial substance by which inclusion is first carried out to such inorganic porosity particles, a thing with a germicidal action and a thing with bacteriostatic action are also contained. As a concrete antibacterial substance, 5-chloro-2-methyl-4-isothia \*\*\*\*\*- 3-one, 2-methyl-4-isothia \*\*\*\*\*- 3-one, 1,2-benziso thiazoline 3-one, 2-n-octyl-4-iso thiazoline 3-one, 2 -(4-thiazolyl)- Benzimidazole. Humulon (humulon), such as an antibiotic, the lupulone (lupulon), Allylsine, allylisothia NETO (allyl isothiocyante), Chlorogenic acid, solanine, the tangeritin (tangeritin), Berberine, hinokitiol, iodine, an extract of a Japanese horseradish, forsythia extract, Rumput roman extract, protamine, methylparaben, ethylparaben, Propylparaben, WANIRIN, thinner MIKKU aldehyde, p-hydroxy benzoate ester, d-limonene, ethyl alcohol, camphor, phenyloxide, p-dichlorobenzene, dimethyl fumarate, hiba oil, hiba arborvitae oil, Chamaecyparis taiwanensis oil, cassia oil, dill oil, lemon oil, citronella oil, clove oil, time oil, linalool, transformer PINOKARU Weor, p-isopropylcyclohexanol. Can FERE nick aldehyde, gamma-decalactone, g undecalactone, Formalin, hypochlorous acid NATORIMU, isopropanol, phenol, A benzalkonium chloride, chlorhexidine, a chloride alkyl diamide ethylglycine, A glutaraldehyde, chlorhexidine glyconate, thiabendazole, 2,4,5,6-tetrachloro isophthal nitril, a benzimidazole system compound, an organic iodine system compound, an organic nitrogen sulfur-systems compound, amino metal silver (product made from incorporated company Japanese ore), etc. are used.

[0014]As an underwater creature antibonding agent, 2-methylthio 4-t-butylamino 6-cyclobutylpropylamino S-triazine, 2,3,5,6-tetrachloro-4 (MACHIRU sulfonyl) pyridine, amino metal copper (product made from incorporated company Japanese ore), chloridation triphenyltin, acetic acid triphenyltin, triphenyltin hydroxide, tributyltin oxide, and TORIPURO pill tin chloride can be mentioned.

[0015]Natural aromatic and synthetic perfume are used as perfume. As the natural aromatic, spearmint oil, peppermint oil, citronella oil, Eucalyptus oil, cascarilla oil, birch oil, cinnamon oil, What combined one sort chosen from clove oil, garlic oil, HAKKAOIRU, Marjoram oil, nutmeg oil, PAL MAROZA oil, SHISOOIRU, rose oil, savory oil, rosemary oil, lavender oil, etc. or two sorts or more is used. As synthetic perfume, amyl acetate, alpha-amylcinnamic aldehyde, Isoamyl salicylate, anisaldehyde, benzyl acetate, benzyl alcohol, What combined one sort chosen from borneol, l-carvone, menthol, citral, citronellal, citronellol, a coumarin, eugenol, a methyl salicylate, vanillin, a terpeneol, etc. or two sorts or more is used. A mixing-natural aromatic and synthetic perfume thing can also carry out inclusion.

[0016]An insecticide, a germicide, a nematocide, miticide, etc. are raised as agricultural chemicals. As a germicide, a dithiocarbamate agent, an organic sulfur (mancozeb etc.) system agent (captan etc.), Organophosphorus compounds (O,O-diisopropyl- S-benzylthio phosphate etc.), chlorinated organic compounds (pentachlorophenol etc.), an organoarsenic pesticide, and aliphatic series halogen (methyl ARUSENIKKUJI methylcarbamate etc.) agents (methyl bromide etc.) are mentioned.

[0017]As an insecticide, organo-phosphoric pesticides (dichlorvos etc.) and the Cava mate system insecticide (1-naphthyl N-methylcarbamate etc.), An organic halogen system insecticide and nicotine (DDT etc.) (nicotine etc.). Oil refinement (cineol, dill oil, Japanese mint oil, eucalyptus oil, TAPENTIN oil, etc.) of fluoroacetamide, pyrethroid (pyrethrine, allethrin, etc.), and vegetable origin, boric acid, etc. are used.

[0018]As miticide, Kelthane, prochlorol, a clo RUBEJI rate, chloropropylate, phenisobromolate, lavender oil, Melissa oil, peppermint oil, salvia oil, rosemary oil, etc. are used.

[0019]As a nematocide, there are a mixture of chloropicrin, 2,3-dichloropropane, and 1,3-dichloropropene, 1,2-dibromomethane, and a methylisocyanate, and a mixture of chloropicrin, 2,3-dichloropropane, and 1,3-dichloropropene, etc. are used preferably.

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OPERATION

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[Function]While carrying out inclusion of what combined one sort chosen as inorganic porosity particles from an antibacterial substance, an underwater creature antibonding agent, perfume, and agricultural chemicals, or two sorts or more, the antibacterial substance, the underwater creature antibonding agent, the perfume, and the agricultural chemicals by which inclusion was carried out also on the conditions under underwater or an elevated temperature by covering with a polymer material -- elution -- it becomes difficult to volatilize. The functional material inclusion was carried out [ functional material ] to inorganic porosity particles by what combined one sort chosen from protein, polysaccharide, a synthetic resin, latex, and steroid as the polymer material or two sorts or more, and the water-soluble thing becomes eluting and being hard to volatilize. When using a water-soluble thing, the adjustment of time after being underwater immersed by adjusting the solubility until said inclusion thing flows out is attained, and it can realize sustained-release [ underwater ].

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EXAMPLE

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[Example]Although the example of this invention is described below, referring to drawings, this invention is not restrained at all by this example.

[0022]Drawing 1 and drawing 2 are the structure table \*\*\*\*\* explanatory views which carried out inclusion of the underwater creature antibonding agent to the centrum, and covered porous silica (trade name: the God ball, the Suzuki oil and fat industry incorporated company make) with gelatin. This is in the state where the minute hole 4 is also filled up with the underwater creature antibonding agent 3 by which inclusion was carried out to the centrum 2 of said porous silica 1, and covers the gelatin 5 only to a peripheral part. Although not illustrated, inclusion of the underwater creature antibonding agent 3 is carried out only to the centrum 2 of said porous silica 1, and while being covered with the gelatin 5, there is also a thing in the state where the minute hole 4 was also filled up with the gelatin 5.

[0023](Example 1) as Example 1 -- porous silica (trade name: -- the God ball.) The powder 20g of seaweed-proofing agent 2,3,5,6-tetrachloro-4 (MACHIRU sulfonyl) pyridine (trade name: made in Densil-S-100 eye SHIAI Japan, Inc.) is melted in the solvent of methyl ethyl ketone as an underwater creature antibonding agent at the Suzuki oil and fat industry incorporated company make 200g, After making said porous silica impregnated, it was made to dry at about 50 \*\* for 2 hours. Thus, the obtained porous silica whole quantity containing a seaweed-proofing agent is distributed in 2 % of the weight of gelatin (trade name: made by gelatin 21 Nitta Gelatin, Inc.) solution 4000g, The porous silica which covered the gelatin containing an underwater creature antibonding agent which carried out coating treatment with gelatin under the conditions of 150 \*\* and 30000 revolutions per minute using the spray dry device (trade name: CL-8 the OHKAWARA KAKOHKI incorporated company make) was obtained.

[0024](Example 2) 200 g (trade name: made by God ball Suzuki oil and fat industry incorporated company) of porous silica which carried out inclusion of the volatile high jasmine perfume liquid 20g as Example 2, methylene chloride -- a solvent -- cholesterol: -- ethyl cellulose: -- it mixing by the ratio of polyethylene-glycol (molecular weight 20000) =1:2:1, distributing in the solution 300g 10% of the weight, and, The porous silica in which there is the scent of the jasmine which performed coating treatment using the vacuum freeze dryer (made in [ for 1 l. ] testing machine Toyo Research Institute, Inc.), and covered it by cholesterol, ethyl cellulose, and a polyethylene glycol was obtained.

[0025](Example 3) As Example 3, 10 g of porous silica which carried out inclusion of the rumpu roman extract 5g as an antibacterial substance, Methanol was distributed in the solution 125g mixed [ 3 % of the weight of ethyl cellulose ] to the solvent, the continuation granulation dryer (made by OHKAWARA KAKOHKI incorporated company) performed granulation desiccation for 10 minutes, and the antibacterial porous silica covered by ethyl cellulose was obtained.

[0026](Comparative examples 1, 2, and 3) What is not performing coating treatment of Examples 1, 2, and 3 was obtained as the comparative examples 1, 2, and 3.



[0027](Test of Example 1 and the comparative example 1) Example 1 and the comparative example 1, Adjust so that it may become 5% of the weight in the acrylic resin system paints which dissolved in xylene, respectively, and the oiliness acrylic resin system paint containing a seaweed-proofing agent is produced, It actually applied to the ship's bottom, the seaweed-proofing test was done by sea immersion, and what observed adhesion of the alga with the naked eye weekly was shown in Table 1 over the period for eight weeks. It has prevented adhesion of the underwater creature of a ship's bottom over the long period of time as it was shown in Table 1, since it was coated by gelatin compared with the comparative example 1 and the rate of dissolution to the inside of sea water was slow Example 1.

[0028]

[Table 1]

船底塗料の防藻テスト結果

	1週目	2週目	3週目	4週目	5週目	6週目	7週目	8週目
実施例1	○	○	○	○	○	○	○	○
比較例1	○	○	×	×	×	×	×	×

○：藻の付着なし

×：藻の付着有り

[0029](Test of Example 2 and the comparative example 2) Example 2 and the comparative example 2, It adjusted so that it might become 5% of the weight in acrylic emulsion system paints, respectively, and the perfume \*\*\*\*\* acrylic emulsion system paint of the jasmine was produced, about 3 g was uniformly applied to plywood of 0.1 mm in thickness, and 5 cm around, and it dried at 20 \*\* for 5 hours. And days until the smell of the perfume is lost by an abuse test deed and organoleptics in the plywood in which the paint was applied with the homoiothermal constant humidity chamber whose temperature inside is 30 \*\* and whose humidity is 90% were shown in Table 2. Since coating treatment is carried out in this example, as it is shown in Table 2 compared with the comparative example 2, the duration in an abuse test is \*\*\*\*\* overwhelmingly.

[0030]

[Table 2]

ジャスミン香料の芳香性試験結果

	1日	2日	3日	4日	5日	6日	7日	8日	9日	10日	11日
実施例2	○	○	○	○	○	○	○	○	○	○	○
比較例2	○	○	○	○	×	×	×	×	×	×	×

○：芳香性有り

×：芳香性なし

[0031](Test of Example 3 and the comparative example 3) Example 3 and the comparative example 3, It adjusted so that it might become 5% of the weight in acrylic emulsion system paints, respectively, and the acrylic emulsion system paint containing an antimicrobial agent was produced, about 2 g was applied to the transparent-acrylic-resin board of 1 cm around at 0.1 mm in thickness, and it dried at the room temperature for 5 hours. It was neglected to the outdoors after that and evaluation of as opposed to [ over the period for eight weeks / weekly ] bacteria and true fungi for

an antibacterial effect was carried out. as the bacteria used for the test -- punishment -- lath subtilis (Bacillus subtilis). Staphylococcus Aureus (Staphylococcus aureus), As Escherichia coli (Escherichia coli), Pseudomonas aeruginosa (Pseudomonas aeruginosa), and true fungi, Aspergillus Nigre (Aspergillus nigar), Aspergillus ORIZE (Aspergillus oryzae), Mucor RUKISHI (Mucor rouxi), Saccharomyces Selby Xie (Saccharomyces cerevisiae) has. An antibacterial test Glucose 1% (w/v) (made by best glucose Wako Pure Chem, Inc.), Yeast extract 2% (w/v) (made by Difco yeast extract Difco), To the GYP liquid medium which was adjusted the pH to 6.8 by peptone 1% (w/v) (made by Difco peptone Difco) of concentration, and it poured distributively 10 cc at a time in each test tube, and carried out sterilization treatment with autoclave. It adjusted so that bacteria and true fungi might become [ g ] in 100,000 pieces /, the acrylic resin plate which did the field test on this was put into in vitro, and bacteria are 37 \*\*, and true fungi were cultivated for three days with the thermostat at 28 \*\*, respectively, and performed growing conditions by macro-scopic observation. Since it was coated with ethyl cellulose and it was not emitted more than needed, its effect was long as Example 3 was shown in Table 3 compared with the comparative example 3.

[0032]

[Table 3]

抗菌テストの結果

供・試 菌		1週目	2週目	3週目	4週目	5週目	6週目	7週目
バチルス サブリリス	実施例1	○	○	○	○	○	○	○
	比較例1	○	○	○	○	×	×	×
スタフィロコッカス アウレウス	実施例1	○	○	○	○	○	○	○
	比較例1	○	○	×	×	×	×	×
大腸菌	実施例1	○	○	○	○	○	○	○
	比較例1	○	○	×	×	×	×	×
シュードモナス フルギダ	実施例1	○	○	○	○	○	○	○
	比較例1	○	○	×	×	×	×	×
アスペルギルス ニガー	実施例1	○	○	○	○	○	○	○
	比較例1	○	○	○	○	×	×	×
アスペルギルス オリゼ	実施例1	○	○	○	○	○	○	○
	比較例1	○	○	○	○	×	×	×
ムコール ルーキ	実施例1	○	○	○	○	○	○	○
	比較例1	○	○	○	×	×	×	×
サッカロマイセス セルビシエ	実施例1	○	○	○	○	○	○	○
	比較例1	○	○	×	×	×	×	×

○：抗菌力有り

×：抗菌力なし

[0033] The example which carried out coating treatment from the above result is shown from a comparative example by Tables 1, 2, and 3 where that effect is continuing over a long period of time

expressed the result of each examination.

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**DESCRIPTION OF DRAWINGS**

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[Brief Description of the Drawings]

[Drawing 1]The section explanatory view of the porous silica of the example of this invention

[Description of Notations]

1. Porous silica
2. Centrum
3. Underwater creature antibonding agent
4. Minute hole
5. Gelatin

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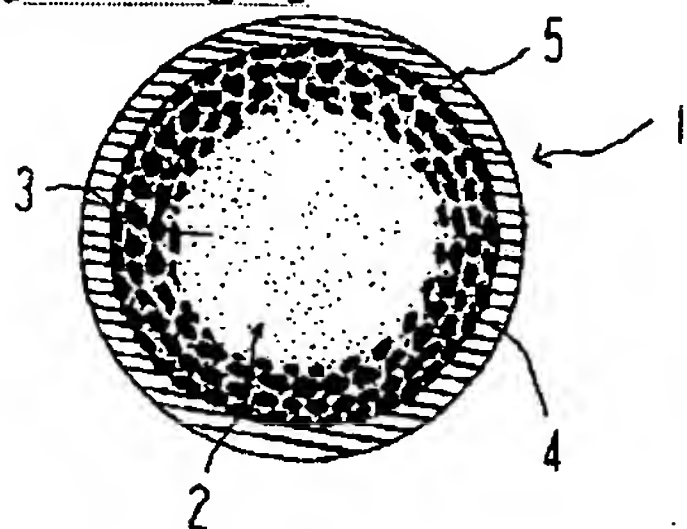
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**DRAWINGS**

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[Drawing 1]



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WRITTEN AMENDMENT

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----- [Written amendment]

[Filing date]February 22, Heisei 6

[Amendment 1]

[Document to be Amended]Specification

[Item(s) to be Amended]Whole sentence

[Method of Amendment]Change

[Proposed Amendment]

[Document Name]Specification

[Title of the Invention]Inorganic porosity particles

[Claim(s)]

[Claim 1]Inorganic porosity particles characterized by covering with a polymer material while carrying out inclusion of what combined one sort chosen from an antibacterial substance, an underwater creature antibonding agent, perfume, and agricultural chemicals, or two sorts or more.

[Claim 2]The inorganic porosity particle according to claim 1 combining one sort chosen from protein, polysaccharide, a synthetic resin, latex, and steroid as said polymer material, or two sorts or more.

[Claim 3]The inorganic porosity particle according to claim 1 or 2, wherein said polymer material is water solubility.

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention is applied to various fields and relates to the inorganic porosity particles which carry out inclusion of the functional material, such as an antibacterial substance, perfume, an underwater creature antibonding agent, and agricultural chemicals.

[0002]

[Description of the Prior Art]Conventionally, what carried out inclusion of the water-soluble and volatile high functional material to inorganic porosity particles, such as porous silica, is used for a ship bottom paint, an underwater creature antibonding agent, and other functional uses as high-performance material. Where inorganic porosity particles are warmed to a various substrate, scour this and it is crowded, or it is mixed to each solvent.

[0003]

[Problem(s) to be Solved by the Invention]Therefore, there was a problem. Namely, if inclusion of the water-soluble and volatile high functional material is carried out to inorganic porosity particles, and it scours to various substrates, such as a paint, ink, and cosmetics, and mixes [ it is crowded or ] to them, When content falls and the functional material by which inclusion must have been carried out actually uses it by elution, volatilization, etc. into a scour lump or a mixing process, when the amount of inclusion decreases, sometimes, there is a problem that effect becomes weak.

[0004]When carrying out inclusion of the underwater creature antibonding agent and using it for a ship bottom paint, by being immersed all over sea water, the underwater creature antibonding agent which carried out inclusion flowed easily, and the problem which is not maintained over a long time also had the underwater creature antisticking effect.

[0005]The purpose of this invention is what was going to improve inorganic porosity particles, and although it scours the high functional material of the water solubility by which inclusion was carried out to inorganic porosity particles, or volatility to a various substrate and is crowded, it tends to provide the inorganic porosity particles to which said functional material by which inclusion was carried out is eluted, and does not volatilize easily.

[0006]

[Means for Solving the Problem]The above-mentioned problem is solved by covering a polymer material to inorganic porosity particles. As a polymer material, and protein, polysaccharide, a synthetic resin, latex, What combined one sort chosen from steroid or two sorts or more is covered, water-soluble gelatin etc. are used as protein, and casein of insoluble in water nature, casein sodium, gluten, etc. are mentioned. A polysaccharide simple substance and its derivative can use as polysaccharide, and Gum arabic of water solubility [ it ], There are gellant gum, hydroxyethyl cellulose, carboxymethyl cellulose, hydroxypropylcellulose, psyllium seed gum, etc., and methyl cellulose of insoluble in water nature, ethyl cellulose, cellulose acetate, curdlan, etc. are mentioned. Poly vinyl alcohol water-soluble in a synthetic resin, a polyethylene glycol, A polypropylene glycol etc. are used and an acrylic resin of insoluble in water nature, polymethylmethacrylate, polyvinyl acetate, polystyrene, Pori Sall John, etc. are possible, As latex, natural rubber latex, styrene butadiene copolymer latex, Polybutadiene latex, acrylonitrile butadiene copolymer latex, polyisoprene latex, polyvinyl acetate latex, polyvinyl chloride acetate copolymer latex, ethylene-vinylacetate copolymer latex, etc. are mentioned. Cholesterol of insoluble in water nature, etc. are mentioned as steroid. A polymer material may be water solubility.

[0007]As a method of coating said polymer material, spray dry, a granulation, vacuum drying, and freeze-drying are mentioned, and it is suitably used according to material.

[0008]As an inorganic compound in which what was excellent in a heatproof, water resistance, and corrosion resistance at inorganic porosity particles used here is desirable, and forms this inorganic porosity particle, It is usable in carbonate of alkaline-earth metals, silicate, phosphate, sulfate, a metallic oxide and metal hydroxide, other metallic silicates, or other metallic carbonate.

[0009]As carbonate of alkaline-earth metals, specifically Calcium carbonate, barium carbonate, carbonic acid -- a mug -- NEUMU etc. -- as the silicate of alkaline-earth metals -- a calcium silicate. barium silicate, a magnesium silicate, etc. -- moreover -- as the phosphate of alkaline-earth metals -- calcium phosphate, barium phosphorate, magnesium phosphate, etc. -- and as sulfate of alkaline-earth metals, calcium sulfate, barium sulfate, magnesium sulfate, etc. are mentioned again, respectively.

[0010]Furthermore, as a metallic oxide, silica, titanium oxide, iron oxide, cobalt oxide, a zinc oxide, nickel oxide, manganese oxide, an aluminum oxide, etc. are mentioned, and iron hydroxide, nickel hydroxide, aluminium hydroxide, calcium hydroxide, chromium hydroxide, etc. are mentioned as metal hydroxide, respectively.

[0011]And zinc silicate, aluminum silicate, etc. are mentioned as other metallic silicates, and zinc carbonate, basic copper carbonate, etc. are mentioned as other metallic carbonate, respectively. It is possible to use inorganic porous silica (trade name: God ball) already preferably marketed by these people.

[0012]A function is given by carrying out inclusion of what combined one sort chosen from an antibacterial substance, an underwater creature antibonding agent, agricultural chemicals, and perfume as functional material by which inclusion is carried out, or two sorts or more.

[0013]As an antibacterial substance by which inclusion is first carried out to such inorganic porosity particles, a thing with a germicidal action and a thing with bacteriostatic action are also contained.

As a concrete antibacterial substance, 5-chloro-2-methyl-4-isothia \*\*\*\*\*- 3-one, 2-methyl-4-isothia \*\*\*\*\*- 3-one, 1,2-benziso thiazoline 3-one, 2-n-octyl-4-iso thiazoline 3-one, 2 -(4-thiazolyl)- Benzimidazole. Humulon (humulon), such as an antibiotic, the lupulone (lupulon), Allylsine, allylisothia NETO (allyl isothiocyante), Chlorogenic acid, solanine, the tangeritin (tangeritin), Berberine, hinokitiol, iodine, an extract of a Japanese horseradish, forsythia extract, Rumpu roman extract, protamine, methylparaben, ethylparaben, Propylparaben, WANIRIN, thinner MIKKU aldehyde, p-hydroxy benzoate ester, d-limonene, ethyl alcohol, camphor, phenyloxide, p-dichlorobenzene, dimethyl fumarate, hiba oil, hiba arborvitae oil, Chamaecyparis taiwanensis oil, cassia oil, dill oil, lemon oil, citronella oil, clove oil, time oil, linalool, transformer PINOKARU Weor, p-isopropylcyclohexanol. Can FERE nick aldehyde, gamma-decalactone, g undecalactone, Formalin, hypochlorous acid NATORIMU, isopropanol, phenol, A benzalkonium chloride, chlorhexidine, a chloride alkyl diamide ethylglycine, A glutaraldehyde, chlorhexidine glyconate, thiabendazole, 2,4,5,6-tetrachloro isophthal nitril, a benzimidazole system compound, an organic iodine system compound, an organic nitrogen sulfur-systems compound, amino metal silver (product made from incorporated company Japanese ore), etc. are used.

[0014]As an underwater creature antibonding agent, 2-methylthio 4-t-butylamino 6-cyclobutylpropylamino S-triazine, 2,3,5,6-tetrachloro-4 (MACHIRU sulfonyl) pyridine, amino metal copper (product made from incorporated company Japanese ore), chloridation triphenyltin, acetic acid triphenyltin, triphenyltin hydroxide, tributyltin oxide, and TORIPURO pill tin chloride can be mentioned.

[0015]Natural aromatic and synthetic perfume are used as perfume. As the natural aromatic, spearmint oil, peppermint oil, citronella oil, Eucalyptus oil, cascarilla oil, birch oil, cinnamon oil, What combined one sort chosen from clove oil, garlic oil, HAKKAOIRU, Marjoram oil, nutmeg oil, PAL MAROZA oil, SHISOOIRU, rose oil, savory oil, rosemary oil, lavender oil, etc. or two sorts or more is used. As synthetic perfume, amyl acetate, alpha-amylcinnamic aldehyde, Isoamyl salicylate, anisaldehyde, benzyl acetate, benzyl alcohol, What combined one sort chosen from borneol, 1-carvone, menthol, citral, citronellal, citronellol, a coumarin, eugenol, a methyl salicylate, vanillin, a terpeneol, etc. or two sorts or more is used. A mixing-natural aromatic and synthetic perfume thing can also carry out inclusion.

[0016]An insecticide, a germicide, a nematocide, miticide, etc. are raised as agricultural chemicals. As a germicide, a dithiocarbamate agent, an organic sulfur (mancozeb etc.) system agent (captan etc.), Organophosphorus compounds (O,O-diisopropyl- S-benzylthio phosphate etc.), chlorinated organic compounds (pentachlorophenol etc.), an organoarsenic pesticide, and aliphatic series halogen (methyl ARUSENIKKUJI methylcarbamate etc.) agents (methyl bromide etc.) are mentioned.

[0017]As an insecticide, organo-phosphoric pesticides (dichlorvos etc.) and the Cava mate system insecticide (1-naphthyl N-methylcarbamate etc.), An organic halogen system insecticide and nicotine (DDT etc.) (nicotine etc.). Oil refinement (cineol, dill oil, Japanese mint oil, eucalyptus oil, TAPENTIN oil, etc.) of fluoroacetamide, pyrethroid (pyrethrine, allethrin, etc.), and vegetable origin, boric acid, etc. are used.

[0018]As miticide, Kelthane, prochlorol, a clo RUBEJI rate, chloropropylate, phenisobromolate, lavender oil, Melissa oil, peppermint oil, salvia oil, rosemary oil, etc. are used.

[0019]As a nematocide, there are a mixture of chloropicrin, 2,3-dichloropropane, and 1,3-dichloropropene, 1,2-dibromomethane, and a methylisocyanate, and a mixture of chloropicrin, 2,3-dichloropropane, and 1,3-dichloropropene, etc. are used preferably.

[0020]

[Function]While carrying out inclusion of what combined one sort chosen as inorganic porosity particles from an antibacterial substance, an underwater creature antibonding agent, perfume, and agricultural chemicals, or two sorts or more, the antibacterial substance, the underwater creature antibonding agent, the perfume, and the agricultural chemicals by which inclusion was carried out also on the conditions under underwater or an elevated temperature by covering with a polymer



material -- elution -- it becomes difficult to volatilize. The functional material inclusion was carried out [ functional material ] to inorganic porosity particles by what combined one sort chosen from protein, polysaccharide, a synthetic resin, latex, and steroid as the polymer material or two sorts or more, and the water-soluble thing becomes eluting and being hard to volatilize. When using a water-soluble thing, the adjustment of time after being underwater immersed by adjusting the solubility until said inclusion thing flows out is attained, and it can realize sustained-release [ underwater ].  
[0021]

[Example] Although the example of this invention is described below, referring to drawings, this invention is not restrained at all by this example.

[0022] Drawing 1 and drawing 2 are the structure table \*\*\*\*\* explanatory views which carried out inclusion of the underwater creature antibonding agent to the centrum, and covered porous silica (trade name: the God ball, the Suzuki oil and fat industry incorporated company make) with gelatin. This is in the state where the minute hole 4 is also filled up with the underwater creature antibonding agent 3 by which inclusion was carried out to the centrum 2 of said porous silica 1, and covers the gelatin 5 only to a peripheral part. Although not illustrated, inclusion of the underwater creature antibonding agent 3 is carried out only to the centrum 2 of said porous silica 1, and while being covered with the gelatin 5, there is also a thing in the state where the minute hole 4 was also filled up with the gelatin 5.

[0023] (Example 1) as Example 1 -- porous silica (trade name: -- the God ball.) The powder 20g of seaweed-proofing agent 2,3,5,6-tetrachloro-4 (MACHIRU sulfonyl) pyridine (trade name: made in Densil-S-100 eye SHIAI Japan, Inc.) is melted in the solvent of methyl ethyl ketone as an underwater creature antibonding agent at the Suzuki oil and fat industry incorporated company make 200g, After making said porous silica impregnated, it was made to dry at about 50 \*\* for 2 hours. Thus, the obtained porous silica whole quantity containing a seaweed-proofing agent is distributed in 2 % of the weight of gelatin (trade name: made by gelatin 21 Nitta Gelatin, Inc.) solution 4000g. The porous silica which covered the gelatin containing an underwater creature antibonding agent which carried out coating treatment with gelatin under the conditions of 150 \*\* and 30000 revolutions per minute using the spray dry device (trade name: CL-8 the OHKAWARA KAKOHKI incorporated company make) was obtained.

[0024] (Example 2) 200 g (trade name: made by God ball Suzuki oil and fat industry incorporated company) of porous silica which carried out inclusion of the volatile high jasmine perfume liquid 20g as Example 2, methylene chloride -- a solvent -- cholesterol: -- ethyl cellulose: -- it mixing by the ratio of polyethylene-glycol (molecular weight 20000) =1:2:1, distributing in the solution 300g 10% of the weight, and, The porous silica in which there is the scent of the jasmine which performed coating treatment using the vacuum freeze dryer (made in [ for 1 l. ] testing machine Toyo Research Institute, Inc.), and covered it by cholesterol, ethyl cellulose, and a polyethylene glycol was obtained.

[0025] (Example 3) As Example 3, 10 g of porous silica which carried out inclusion of the rumpu roman extract 5g as an antibacterial substance, Methanol was distributed in the solution 125g mixed [ 3 % of the weight of ethyl cellulose ] to the solvent, the continuation granulation dryer (made by OHKAWARA KAKOHKI incorporated company) performed granulation desiccation for 10 minutes, and the antibacterial porous silica covered by ethyl cellulose was obtained.

[0026] (Comparative examples 1, 2, and 3) What is not performing coating treatment of Examples 1, 2, and 3 was obtained as the comparative examples 1, 2, and 3.

[0027] (Test of Example 1 and the comparative example 1) Example 1 and the comparative example 1, Adjust so that it may become 5% of the weight in the acrylic resin system paints which dissolved in xylene, respectively, and the oiliness acrylic resin system paint containing a seaweed-proofing agent is produced, It actually applied to the ship's bottom, the seaweed-proofing test was done by sea immersion, and what observed adhesion of the alga with the naked eye weekly was shown in Table 1 over the period for eight weeks. It has prevented adhesion of the underwater creature of a

ship's bottom over the long period of time as it was shown in Table 1, since it was coated by gelatin compared with the comparative example 1 and the rate of dissolution to the inside of sea water was slow Example 1.

[0028]

[Table 1]

[0029](Test of Example 2 and the comparative example 2) Example 2 and the comparative example 2, It adjusted so that it might become 5% of the weight in acrylic emulsion system paints, respectively, and the perfume \*\*\*\*\* acrylic emulsion system paint of the jasmine was produced, about 3 g was uniformly applied to plywood of 0.1 mm in thickness, and 5 cm around, and it dried at 20 \*\* for 5 hours. And days until the smell of the perfume is lost by an abuse test deed and organoleptics in the plywood in which the paint was applied with the homoiothermal constant humidity chamber whose temperature inside is 30 \*\* and whose humidity is 90% were shown in Table 2. Since coating treatment was carried out in this example, as shown in Table 2, compared with the comparative example 2, the duration in the abuse test was overwhelmingly long. The duration of perfume was the same also in the plywood which is more thick.

[0030]

[Table 2]

[0031](Test of Example 3 and the comparative example 3) Example 3 and the comparative example 3 were adjusted so that it might become 5% of the weight in acrylic emulsion system paints, respectively, they produced the acrylic emulsion system paint containing an antimicrobial agent, applied about 2 g to the transparent-acrylic-resin board of 1 cm around, and dried it at the room temperature for 5 hours. It was neglected to the outdoors after that and evaluation of as opposed to [ over the period for eight weeks / weekly ] bacteria and true fungi for an antibacterial effect was carried out. as the bacteria used for the test -- punishment -- lath subtilis (*Bacillus subtilis*), *Staphylococcus Aureus* (*Staphylococcus aureus*), *Escherichia coli* (*Escherichia coli*), *Pseudomonas aeruginosa* (*Pseudomonas aeruginosa*), and true fungi, *Aspergillus Nigre* (*Aspergillus niger*), *Aspergillus ORIZE* (*Aspergillus oryzae*), *Mucor RUKISHI* (*Mucor rouxi*), *Saccharomyces Selby Xie* (*Saccharomyces cerevisiae*) has. An antibacterial test Glucose 1% (w/v) (made by best glucose Wako Pure Chem, Inc.), Yeast extract 2% (w/v) (made by Difco yeast extract Difco), To the GYP liquid medium which was adjusted the pH to 6.8 by peptone 1% (w/v) (made by Difco peptone Difco) of concentration, and it poured distributively 10 cc at a time in each test tube, and carried out sterilization treatment with autoclave. It adjusted so that bacteria and true fungi might become [ g ] in 100,000 pieces /, the acrylic resin plate which did the field test on this was put into in vitro, and bacteria are 37 \*\*, and true fungi were cultivated for three days with the thermostat at 28 \*\*, respectively, and performed growing conditions by macro-scopic observation. Since it was coated with ethyl cellulose and it was not emitted more than needed, its effect was long as Example 3 was shown in Table 3 compared with the comparative example 3.

[0032]

[Table 3]

[0033]The example which carried out coating treatment from the above result is shown from a comparative example by Tables 1, 2, and 3 where that effect is continuing over a long period of time expressed the result of each examination.

[0034]

[Effect of the Invention]By covering a polymer material, they can be prevented from the antibacterial substance, the underwater creature antibonding agent, the perfume, and the agricultural chemicals by which inclusion was carried out being eluted for a short time more than needed, or volatilizing, and an effect can be maintained over a long period of time. A good result is obtained by furthermore using what combined one sort chosen from protein, polysaccharide, a synthetic resin, latex, and steroid, or two sorts or more, and a water-soluble thing as a polymer material. When a water-soluble thing is used especially, adjustment of time after being underwater

immersed by adjusting the solubility until said thing which carried out inclusion flows out can be attained, sustained-release [ underwater ] can be realized, and the effect outstanding as a ship bottom paint, or a seaweed-proofing agent and a lasting long aromatic can be demonstrated.

[Brief Description of the Drawings]

[Drawing 1]The section explanatory view of the porous silica of the example of this invention

[Description of Notations]

1. Porous silica
2. Centrum
3. Underwater creature antibonding agent
4. Minute hole
5. Gelatin

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[Translation done.]

(19) 日本国特許庁 (JP)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平7-173452

(43) 公開日 平成7年(1995)7月11日

(51) Int. Cl. <sup>6</sup>	識別記号	片内整理番号	PI	技術表示箇所
C09K 3/00	110 B			
A01N 25/00	101			
25/26				
B01J 13/04				
9342-4G B01J 13/02 A				
審査請求 未請求 請求項の数3 FD (全10頁) 最終頁に続く				

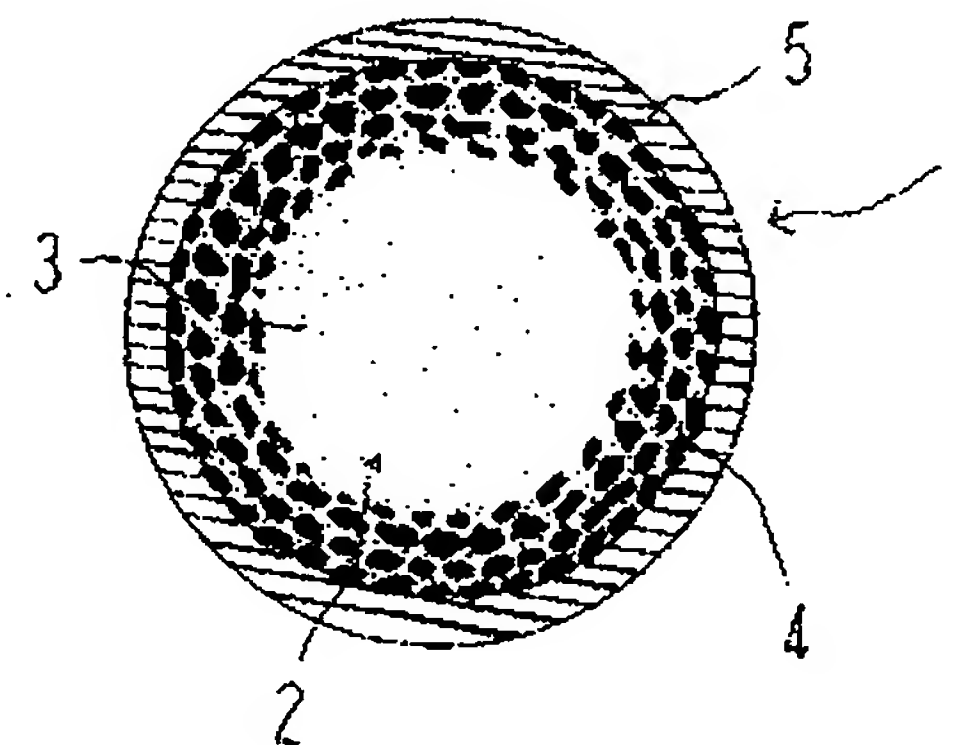
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(54) 【発明の名称】 無機多孔質微粒子

(57) 【要約】

【目的】 無機多孔質微粒子に包接された水溶性や揮発性の高い機能性物質を各種基材に練り混んでも包接された前記機能性物質が容易に溶出や揮発しない無機多孔質微粒子を提供しようとする。

【構成】 高分子材料やタンパク質、多糖、合成樹脂、ラテックスから選んだ1種または2種以上を組合わせたものを外被したりあるいは水溶性の高分子を外被した無機多孔質微粒子。





(2)

特開平7-173452

1

2

## 【特許請求の範囲】

【請求項1】抗菌性物質、水中生物付着防止剤、香料、農薬から選んだ1種または2種以上を組合わせたものを包接するとともに、高分子材料で外被したことを特徴とする無機多孔質微粒子。

【請求項2】前記高分子材料としてタンパク質、多糖類、合成樹脂、ラテックス、ステロイドから選んだ1種または2種以上を組合わせたことを特徴とする請求項1記載の無機多孔質微粒子。

【請求項3】前記高分子材料が水溶性であることを特徴とする請求項1または2記載の無機多孔質微粒子。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は、様々な分野に応用され、抗菌性物質、香料、水中生物付着防止剤、農薬等の機能性物質を包接する無機多孔質微粒子に関する。

## 【0002】

【従来の技術】従来、機能性材料として、多孔質シリカ等の無機多孔質微粒子に水溶性や揮発性の高い機能性物質を包接したものが、船底塗料や水中生物付着防止剤、その他の機能用途に用いられている。これは無機多孔質微粒子を各種基材に加温した状態で練り混ぜたり、各溶剤に混合していたものである。

## 【0003】

【発明が解決しようとする課題】そのため問題があった。即ち、無機多孔質微粒子に水溶性や揮発性の高い機能性物質を包接して塗料、インキ、化粧品等の各種基材に練り混ぜたり混合したりすると、練り込みや混合工程中に、包接されたはずの機能性物質が溶出や揮発などで含有率が下がり、実際に使用すると時には包接量が減少することにより効力が弱くなるという問題がある。

【0004】また水中生物付着防止剤を包接して船底塗料に用いる際には、海水中に浸漬することによって包接した水中生物付着防止剤が容易に溶けてしまい、水中生物付着防止効果が長時間に渡って持続しない問題もあった。

【0005】本発明の目的は、無機多孔質微粒子の改良をおこなわんとしたもので、無機多孔質微粒子に包接された水溶性や揮発性の高い機能性物質を各種基材に練り混ぜても、包接された前記機能性物質が容易に溶出や揮発しない無機多孔質微粒子を提供しようとするものである。

## 【0006】

【課題を解決するための手段】上記問題は、無機多孔質微粒子に高分子材料を外被することによって解決される。そして、高分子材料としてはタンパク質、多糖類、合成樹脂、ラテックス、ステロイドから選んだ1種または2種以上を組合わせたものを外被するものであり、タンパク質としては水溶性のゼラチン等が用いられ、水不溶性のカゼイン、カゼインナトリウム、グルテン等が夢

げられる。また多糖類としては多糖類単体やその誘導体を用いることができ、それには水溶性のアラビアガム、ジェランガム、ヒドロキシエチルセルロース、カルボキシメチルセルロース、ヒドロキシプロピルセルロース、サイリウムシードガム等があり、水不溶性のメチルセルロース、エチルセルロース、酢酸セルロース、カードラン等が挙げられる。さらに、合成樹脂では水溶性のポリビニールアルコール、ポリエチレングリコール、ポリプロピレングリコール等が用いられ、水不溶性のアクリル樹脂、ポリメチルメタアクリレート、ポリ酢酸ビニル、ポリスチレン、ポリサルフォン等が可能で、ラテックスとしては、天然ゴムラテックス、スチレン-ブタジエン共重合体ラテックス、ポリブタジエンラテックス、アクリロニトリル-ブタジエン共重合体ラテックス、ポリイソブレンラテックス、ポリ酢酸ビニルラテックス、塩化ビニル-酢酸ビニル共重合体ラテックス、エチレン-酢酸ビニル共重合体ラテックス等が挙げられる。ステロイドとしては、水不溶性のコレステロール等が挙げられる。さらに、高分子材料が水溶性であってもよい。

【0007】前記高分子材料をコーティングする方法としてはスプレードライ、造粒、真空乾燥、真空凍結乾燥が挙げられ、材料に応じて適宜使用される。

【0008】ここに用いられる無機多孔質微粒子には耐熱、耐水、耐食性に優れたものが望ましく、この無機多孔質微粒子を形成する無機化合物としては、アルカリ土類金属の炭酸塩、珪酸塩、リン酸塩、硫酸塩や金属酸化物、金属水酸化物、その他の金属珪酸塩、あるいはその他の金属炭酸塩等が使用可能である。

【0009】具体的には、アルカリ土類金属の炭酸塩としては炭酸カルシウム、炭酸バリウム、炭酸マグネシウム等が、アルカリ土類金属の珪酸塩としては珪酸カルシウム、珪酸バリウム、珪酸マグネシウム等が、またアルカリ土類金属のリン酸塩としてはリン酸カルシウム、リン酸バリウム、リン酸マグネシウム等が、そしてまたアルカリ土類金属の硫酸塩としては硫酸カルシウム、硫酸バリウム、硫酸マグネシウム等がそれぞれ挙げられる。

【0010】さらに金属酸化物としてはシリカ、酸化チタン、酸化鉄、酸化コバルト、酸化亜鉛、酸化ニッケル、酸化マンガン、酸化アルミニウム等が、金属水酸化物としては水酸化鉄、水酸化ニッケル、水酸化アルミニウム、水酸化カルシウム、水酸化クロム等がそれぞれ挙げられる。

【0011】そしてその他の金属珪酸塩としては珪酸亜鉛、珪酸アルミニウム等が、その他の金属炭酸塩としては炭酸亜鉛、塩基性炭酸銅等がそれぞれ挙げられる。好ましくは本出願人によってすでに市販されている無機多孔質シリカ（商品名：ゴッドボール）を用いることが可能である。

【0012】包接される機能性物質としては抗菌性物質、水中生物付着防止剤、農薬、香料から選んだ1種ま



(3)

特開平7-173452

3

4

たは2種以上を組合わせたものを包接することによって機能が付与される。

【0013】まずこのような無機多孔質微粒子に包接される抗菌性物質としては、殺菌作用のあるものや酵母作用のあるものも含まれる。具体的な抗菌性物質としては、5-クロロ-2-メチル-4-イソチアゾリノン-3-オン、2-メチル-4-イソチアゾリノン-3-オン、1,2-ベンズイソチアゾリノン-3-オン、2-n-オクチル-4-イソチアゾリノン-3-オン、2-(4-チアゾリル)-ベンズイミダゾール、抗生物質等、ヒュムロン(humulon)、ルブロン(lupulon)、アリシン、アリルイソチアネート(allyl isothiocyanate)、クロロゲン酸、ソラニン、タンゲリチン(tangeritin)、ベルベリン、ヒノキチオール、ヨウ素、ワサビの抽出物、レンギョウ抽出物、カワラヨモギ抽出物、プロタミン、メチルパラベン、エチルパラベン、プロピルパラベン、ワニリン、シンナミックアルデヒド、p-ヒドロキシ安息香酸エステル、d-リモネン、エチルアルコール、カンファー、フェニルオキシド、p-ジクロロベンゼン、ジメチルフマレート、ヒバオイル、アスナロオイル、タイワンヒノキオイル、カシアオイル、ディルオイル、レモンオイル、シトロネラオイル、クローブオイル、タイムオイル、リナロール、トランス-β-イソカルベオール、p-イソプロピルシクロヘキサノール、カンフェレニックアルデヒド、γ-デカラクトン、γ-ウンデカラクトン、ホルマリン、次亜塩素酸ナトリウム、イソプロパノール、フェノール、塩化ベンザルコニウム、クロルヘキシジン、塩酸アルキルジアミドエチルグリシン、グルタルアルデヒド、グルコン酸クロルヘキシジン、チアベンダゾール、2,4,5,6-テトラクロロイソフタルニトリル、ベンズイミダゾール系化合物、有機ヨウ素系化合物、有機窒素硫黄系化合物、アミノメタル銀(株式会社日鉱製)等が用いられる。

【0014】水中生物付着防止剤としては2-メチルチオ-4-1-ブチルアミノ-6-シクロプロピルアミノ-S-トリアジン、2,3,5,6-テトラクロロ-4-(マチルスルフォニル)ピリジン、アミノメタル銅(株式会社日鉱製)、塩化トリフェニルスズ、酢酸トリフェニルスズ、水酸化トリフェニルスズ、トリブチルスズオキサイド、塩化トリプロピルスズを挙げられる。

【0015】さらに、香料としては天然香料や合成香料が用いられる。その天然香料としてスベアミントオイル、ペパーミントオイル、シトロネラオイル、ユーカリオイル、カスカリラオイル、バーチオイル、シナモンオイル、クローブオイル、ニンニクオイル、ハッカオイル、マジョラムオイル、ナツメグオイル、パルマローザオイル、シソオイル、ローズオイル、セイボリオイル、ローズマリーオイル、ラベンダーオイル等から選んだ1種または2種以上を組合わせたものが用いられる。合成

香料としては、酢酸アミル、α-アミルシンナミックアルデヒド、サリチル酸イソアミル、アニスアルデヒド、酢酸ベンジル、ベンジルアルコール、ボルネオール、1-カルボン、メントール、シトラール、シトロネラール、シトロネロール、クマリン、オイゲノール、サリチル酸メチル、バニリン、テルピネオール等から選んだ1種または2種以上を組合わせたものが用いられる。また、天然香料や合成香料を混合したものも包接することが可能である。

【0016】農薬としては、殺虫剤、殺菌剤、殺線虫剤、殺ダニ剤等があげられる。殺菌剤としてはチチオカーバメイト剤(マンゼブ等)、有機硫黄系剤(キャプタン等)、有機リン系剤(O,O-ジイソプロピル-S-ベンジルチオホスフェート等)、有機塩素系剤(ペンタクロロフェノール等)、有機ヒ素系剤(メチルアルセニックジメチルカーバメイト等)、脂肪族ハロゲン系剤(臭化メチル等)が挙げられる。

【0017】また殺虫剤としては、有機リン系殺虫剤(ジクロルボス等)やカーバメイト系殺虫剤(1-ナフチル-N-メチルカーバメイト等)、有機ハロゲン系殺虫剤(ディーディーティ等)、ニコチン類(ニコチン等)、フルオロ酢酸アミド、ピレスロイド類(ピレスリン、アレスリン等)、植物由来の精油(シネオール、ディルオイル、日本ハッカオイル、ユーカリオイル、ターペントインオイル等)、ホウ酸等が用いられる。

【0018】殺ダニ剤としては、ケルセン、プロクロノール、クロルベジレート、クロルプロビレート、フェニソプロモレート、ラベンダーオイル、メリッサオイル、ペパーミントオイル、サルビアオイル、ローズマリーオイル等が用いられる。

【0019】殺線虫剤としては、クロルピクリン、2,3-ジクロロプロパンと1,3-ジクロロプロベンの混合物、1,2-ジプロモメタン、メチルイソシアネートがあり好ましくは、クロルピクリン、2,3-ジクロロプロパンと1,3-ジクロロプロベンの混合物等が用いられる。

【0020】

【作用】無機多孔質微粒子に抗菌性物質、水中生物付着防止剤、香料、農薬から選んだ1種または2種以上を組合わせたものを包接するとともに、高分子材料で外被することによって、水中や高温下の条件においても包接された抗菌性物質、水中生物付着防止剤、香料、農薬が溶出や揮発しにくくなる。また、その高分子材料としてはタンパク質、多糖類、合成樹脂、ラテックス、ステロイドから選んだ1種または2種以上を組合わせたものや水溶性のものによっても無機多孔質微粒子に包接された機能性物質が溶出や揮発されにくくなる。また、水溶性のものを用いる場合には、その溶解性を調整することにより水中に浸漬してから前記包接物が流出するまでの時間が調整が可能となり、水中における徐放性が実現でき

(4)

特開平7-173452

5

5

る。

【0021】

【実施例】以下本発明の実施例を図面を参照しながら説明するが、本発明は本実施例に何ら制約されることはない。

【0022】図1及び図2は、水中生物付着防止剤を中空部に包接してゼラチンで多孔質シリカ（商品名：ゴッドボール、鈴木油脂工業株式会社製）を外被した構造表す断面説明図である。これは、前記多孔質シリカ1の中空部2に包接された水中生物付着防止剤3が微小空孔4にも充填されている状態で、外周部のみにゼラチン5を外被したものである。また、図示していないが、前記多孔質シリカ1の中空部2のみに水中生物付着防止剤3が包接され、ゼラチン5で外被されるとともに微小空孔4にもゼラチン5が充填された状態のものもある。

【0023】（実施例1）実施例1として、多孔質シリカ（商品名：ゴッドボール、鈴木油脂工業株式会社製）200gに水中生物付着防止剤として防藻剤2、3、5、6-テトラクロロ-4（マチルスルホン）ピリジン（商品名：Densil-S-100アイシアイジャパン株式会社製）の粉末20gをメチルエチルケトンの溶媒に溶かして、前記多孔質シリカに含浸させた後に、約50℃で2時間乾燥させた。このようにして得られた防藻剤入り多孔質シリカ全量をゼラチン（商品名：ゼラチン21、新田ゼラチン株式会社製）2重量%水溶液4000gに分散し、スプレードライ装置（商品名：CL-8、大川原化工機株式会社製）を使用して150℃、30000回転/分の条件下でゼラチンでコーティング処理した水中生物付着防止剤入りゼラチンを外被した多孔質シリカを得た。

【0024】（実施例2）実施例2として、揮発性の高いジャスミン香料液20gを包接した多孔質シリカ20\*

船底塗料の防藻テスト結果

	1週目	2週目	3週目	4週目	5週目	6週目	7週目	8週目
実施例1	○	○	○	○	○	○	○	○
比較例1	○	○	×	×	×	×	×	×

○：藻の付着なし  
×：藻の付着有り

【0029】（実施例2及び比較例2のテスト）実施例2及び比較例2は、アクリルエマルジョン系塗料に夫々5重量%になるように調整し、ジャスミンの香料入ったアクリルエマルジョン系塗料を作製して、厚さ0.1mm、5cm四方のベニヤ板に約3gを均一に塗布して、5時間20℃で乾燥した。そして、塗料が塗布されたベニヤ板を室内温度が30℃、湿度が90%の恒温恒湿槽

\*0g（商品名：ゴッドボール、鈴木油脂工業株式会社製）を、メチレンクロライドを溶媒にコレステロール：エチルセルロース：ポリエチレングリコール（分子重2000）＝1：2：1の比で混合して10重量%溶液300gに分散し、それを真空凍結乾燥機（1リットル用試験機、東洋技研株式会社製）を用いてコーティング処理を行い、コレステロール、エチルセルロース、ポリエチレングリコールにより外被したジャスミンの香りがする多孔質シリカを得た。

【0025】（実施例3）実施例3として、抗菌性物質としてカワラヨモギ抽出物5gを包接した多孔質シリカ10gを、メタノールを溶媒にエチルセルロース3重量%混合した溶液125gに分散し、連続造粒乾燥機（大川原化工機株式会社製）により10分間造粒乾燥を行い、エチルセルロースで外被した抗菌性多孔質シリカを得た。

【0026】（比較例1、2、3）比較例1、2、3として、実施例1、2、3のコーティング処理を行っていないものを得た。

【0027】（実施例1及び比較例1のテスト）実施例1及び比較例1は、キシレンに溶解したアクリル樹脂系塗料に夫々5重量%になるように調整し、防藻剤入り油性アクリル樹脂系塗料を作製して、実際に船底に塗布をおこなって海中浸漬により防藻テストを行い、8週間の期間に渡って、1週間毎に藻の付着を肉眼により観察したものを表1に示した。実施例1は比較例1と比べてゼラチンによってコーティングされているので海中への溶出速度が遅くなっているため表1に示すとおり、船底の水中生物の付着を長期間に渡って防止できた。

30 【0028】

【表1】

にて虐待テストを行い、官能試験によりその香料の匂いなくなるまでの日数を表2に示した。本例ではコーティング処理しているために比較例2と比べて、表2に示すように、虐待テストでの持続期間は圧倒的に長った。

【0030】

【表2】

(5)

特開平7-173452

7

8

## ジャスミン香料の芳香性試験結果

	1日	2日	3日	4日	5日	6日	7日	8日	9日	10日	11日
実施例2	○	○	○	○	○	○	○	○	○	○	○
比較例2	○	○	○	○	×	×	×	×	×	×	×

○: 芳香性有り

×: 芳香性なし

【0031】(実施例3及び比較例3のテスト) 実施例3及び比較例3は、アクリルエマルジョン系塗料に夫々5重量%になるように調整し、抗菌剤の入ったアクリルエマルジョン系塗料を作製して、厚さ0.1mmで1cm四方の透明アクリル樹脂板に約2gを塗布して、室温で5時間乾燥した。その後屋外に放置して、抗菌効果を8週間の期間に渡って、1週間ごとに細菌類及び真菌類に対する評価をした。そのテストに用いられた細菌類としては、バチラス サブチリス (*Bacillus subtilis*)、スタフィロコッカス アウレウス (*Staphylococcus aureus*)、大腸菌 (*Escherichia coli*)、シュードモナス アエルギノサ (*Pseudomonas aeruginosa*)、また、真菌類としては、アスペルギルス ニガー (*Aspergillus niger*)、アスペルギルス オリゼ (*Aspergillus oryzae*)、ムコール ルーキシ (*Mucor rouxi*)、サッカロマイセス セルビシエ (*Sa*

*ccharomyces cerevisiae*)がある。抗菌テストは、グルコース1% (w/v) (特級グルコース 和光純薬株式会社製)、イーストエキストラクト2% (w/v) (ディフコイーストエキストラクト ディフコ社製)、ペプトン1% (w/v) (ディフコペプトン ディフコ社製)の濃度でpH6.8に調整して10ccずつ各試験管に分注してオートクレーブにより滅菌処理したGYP液体培地に、細菌類及び真菌類が10万個/gになるように調整して、これに、フィールドテストを行ったアクリル樹脂板を試験管内に入れ、細菌類は37℃で、真菌類は28℃で夫々恒温槽にて3日間培養して、生育状況を肉眼観察によりおこなった。実施例3はエチルセルロースでコーティングされているために必要以上には放出しないので、比較例3と比べて表3に示すとおり効果が長かった。

【0032】

【表3】

(6)

特開平7-173452

9

10

抗菌テストの結果

供試品		1週目	2週目	3週目	4週目	5週目	6週目	7週目
実施例1	実施例1	○	○	○	○	○	○	○
	比較例1	○	○	○	○	×	×	×
実施例2	実施例2	○	○	○	○	○	○	○
	比較例2	○	○	×	×	×	×	×
実施例3	実施例3	○	○	○	○	○	○	○
	比較例3	○	○	×	×	×	×	×
実施例4	実施例4	○	○	○	○	○	○	○
	比較例4	○	○	×	×	×	×	×
実施例5	実施例5	○	○	○	○	○	○	○
	比較例5	○	○	×	×	×	×	×
実施例6	実施例6	○	○	○	○	○	○	○
	比較例6	○	○	○	○	×	×	×
実施例7	実施例7	○	○	○	○	○	○	○
	比較例7	○	○	○	○	×	×	×
実施例8	実施例8	○	○	○	○	○	○	○
	比較例8	○	○	○	×	×	×	×
実施例9	実施例9	○	○	○	○	○	○	○
	比較例9	○	○	×	×	×	×	×

○：抗菌力有り

×：抗菌力無し

【0033】以上の結果より、コーティング処理した実施例のほうが比較例より効力が長期間に渡って持続していることが各試験の結果を表した表1、2、3により示される。

【0034】

【発明の効果】高分子材料を外被することにより、包接された抗菌性物質、水中生物付着防止剤、香料、農薬が必要以上に短時間で溶出したり揮発したりすることを防止して、長期間に渡って効果を持続することが出来る。さらに高分子材料としてはタンパク質、多糖類、合成樹脂、ラテックス、ステロイドから選んだ1種または2種以上を組合わせたものや水溶性のものを用いることにより、良好な結果が得られる。特に、水溶性のものを用い

た場合には、その溶解性を調整することにより水中に浸漬してから前記包接した物が溶出するまでの時間の調整が可能となり、水中における徐放性の実現でき、船底塗料や防藻剤及び持続性の長い芳香剤としてすぐれた効果を発揮できる。

【図面の簡単な説明】

【図1】本発明の実施例の多孔質シリカの断面説明図

【符号の説明】

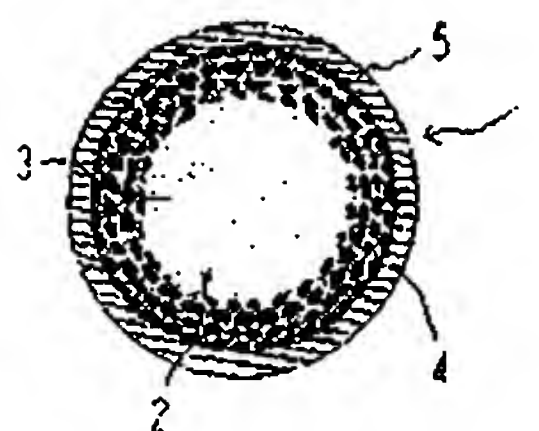
1. 多孔質シリカ
2. 中空部
3. 水中生物付着防止剤
4. 微小空孔
5. ゼラチン



(7)

特開平7-173452

【図1】



## 【手続補正書】

【提出日】平成6年2月22日

## 【手続補正1】

【補正対象書類名】明細書

【補正対象項目名】全文

【補正方法】変更

【補正内容】

【書類名】明細書

【発明の名称】無機多孔質微粒子

【特許請求の範囲】

【請求項1】抗菌性物質、水中生物付着防止剤、香料、農薬から選んだ1種または2種以上を組合わせたものを包接するとともに、高分子材料で外被したことを特徴とする無機多孔質微粒子。

【請求項2】前記高分子材料としてタンパク質、多糖類、合成樹脂、ラテックス、ステロイドから選んだ1種または2種以上を組合わせたことを特徴とする請求項1記載の無機多孔質微粒子。

【請求項3】前記高分子材料が水溶性であることを特徴とする請求項1または2記載の無機多孔質微粒子。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、様々な分野に応用され、抗菌性物質、香料、水中生物付着防止剤、農薬等の機能性物質を包接する無機多孔質微粒子に関する。

【0002】

【従来の技術】従来、機能性材料として、多孔質シリカ等の無機多孔質微粒子に水溶性や揮発性の高い機能性物質を包接したものが、船底塗料や水中生物付着防止剤、その他の機能用途に用いられている。これは無機多孔質微粒子を各種基材に加湿した状態で練り混ぜたり、各溶剤に混合していたものである。

【0003】

【発明が解決しようとする課題】そのため問題があった。即ち、無機多孔質微粒子に水溶性や揮発性の高い機能性物質を包接して塗料、インキ、化粧品等の各種基材に練り混ぜたり混合したりすると、練り込みや混合工程中に、包接されたはずの機能性物質が溶出や揮発などで

含有率が下がり、実際に使用すると時には包接量が減少することにより効力が弱くなるという問題がある。

【0004】また水中生物付着防止剤を包接して船底塗料に用いる際には、海中に浸漬することによって包接した水中生物付着防止剤が容易に溶れてしまい、水中生物付着防止効果が長時間に渡って持続しない問題もあった。

【0005】本発明の目的は、無機多孔質微粒子の改良をおこなわんとしたもので、無機多孔質微粒子に包接された水溶性や揮発性の高い機能性物質を各種基材に練り混ぜても、包接された前記機能性物質が容易に溶出や揮発しない無機多孔質微粒子を提供しようとするものである。

【0006】

【課題を解決するための手段】上記問題は、無機多孔質微粒子に高分子材料を外被することによって解決される。そして、高分子材料としてはタンパク質、多糖類、合成樹脂、ラテックス、ステロイドから選んだ1種または2種以上を組合わせたものを外被するものであり、タンパク質としては水溶性のゼラチン等が用いられ、水不溶性のカゼイン、カゼインナトリウム、グルテン等が挙げられる。また多糖類としては多糖類単体やその誘導体が用いことができ、それには水溶性のアラビアガム、ジェランガム、ヒドロキシエチルセルロース、カルボキシメチルセルロース、ヒドロキシプロピルセルロース、サイリウムシードガム等が有り、水不溶性のメチルセルロース、エチルセルロース、酢酸セルロース、カードラン等が挙げられる。さらに、合成樹脂では水溶性のポリビニールアルコール、ポリエチレングリコール、ポリプロピレングリコール等が用いられ、水不溶性のアクリル樹脂、ポリメチルメタアクリレート、ポリ酢酸ビニル、ポリスチレン、ポリサルフォン等が可能で、ラテックスとしては、天然ゴムラテックス、スチレン-ブタジエン共重合体ラテックス、ポリブタジエンラテックス、アクリロニトリル-ブタジエン共重合体ラテックス、ポリイソブレンラテックス、ポリ酢酸ビニルラテックス、塩化ビニル-酢酸ビニル共重合体ラテックス、エチレン-酢



(8)

特開平7-173452

酸ビニル共重合体ラテックス等が挙げられる。ステロイドとしては、水不溶性のコレステロール等が挙げられる。さらに、高分子材料が水溶性であってもよい。

【0007】前記高分子材料をコーティングする方法としてはスプレードライ、造粒、真空乾燥、真空凍結乾燥が挙げられ、材料に応じて適宜使用される。

【0008】ここに用いられる無機多孔質微粒子には耐熱、耐水、耐食性に優れたものが望ましく、この無機多孔質微粒子を形成する無機化合物としては、アルカリ土類金属の炭酸塩、珪酸塩、磷酸塩、硫酸塩や金属酸化物、金属水酸化物、その他の金属珪酸塩、あるいはその他の金属炭酸塩等が使用可能である。

【0009】具体的には、アルカリ土類金属の炭酸塩としては炭酸カルシウム、炭酸バリウム、炭酸マグネシウム等が、アルカリ土類金属の珪酸塩としては珪酸カルシウム、珪酸バリウム、珪酸マグネシウム等が、またアルカリ土類金属の磷酸塩としては磷酸カルシウム、磷酸バリウム、磷酸マグネシウム等が、そしてまたアルカリ土類金属の硫酸塩としては硫酸カルシウム、硫酸バリウム、硫酸マグネシウム等がそれぞれ挙げられる。

【0010】さらに金属酸化物としてはシリカ、酸化チタン、酸化鉄、酸化コバルト、酸化亜鉛、酸化ニッケル、酸化マンガン、酸化アルミニウム等が、金属水酸化物としては水酸化鉄、水酸化ニッケル、水酸化アルミニウム、水酸化カルシウム、水酸化クロム等がそれぞれ挙げられる。

【0011】そしてその他の金属珪酸塩としては珪酸亜鉛、珪酸アルミニウム等が、その他の金属炭酸塩としては炭酸亜鉛、塩基性炭酸銅等がそれぞれ挙げられる。好ましくは本出願人によってすでに市販されている無機多孔質シリカ（商品名：ゴッドボール）を用いることが可能である。

【0012】包接される機能性物質としては抗菌性物質、水中生物付着防止剤、農薬、香料から選んだ1種または2種以上を組合わせたものを包接することによって機能が付与される。

【0013】まずこのような無機多孔質微粒子に包接される抗菌性物質としては、殺菌作用のあるものや酵母作用のあるものも含まれる。具体的な抗菌性物質としては、5-クロロ-2-メチル-4-イソチアゾリン-3-オン、2-メチル-4-イソチアゾリン-3-オン、1,2-ベンズイソチアゾリン-3-オン、2-n-オクチル-4-イソチアゾリン-3-オン、2-(4-チアゾリル)-ベンズイミダゾール、抗生物質等、ヒュムロン(humulon)、ルブロン(lupulon)、アリシン、アリルイソチアネート(allyl isothiocyanate)、クロロゲン酸、ソラニン、タンゲリチン(tangeretin)、ベルベリン、ヒノキチオール、ヨウ素、ワサビの抽出物、レンギョウ抽出物、カワラヨモギ抽出物、プロタミン、メチル

パラベン、エチルパラベン、プロピルパラベン、ワニリン、シンナミックアルデヒド、p-ヒドロキシ安息香酸エステル、d-リモネン、エチルアルコール、カンファー、フェニルオキシド、p-ジクロルベンゼン、ジメチルフマレート、ヒバオイル、アスナロオイル、タイワンヒノキオイル、カシアオイル、ディルオイル、レモンオイル、シトロネラオイル、クローブオイル、タイムオイル、リナロール、トランス-β-カルベオール、p-イソプロピルシクロヘキサノール、カンフェレニックアルデヒド、γ-デカラクトン、γ-ウンデカラクトン、ホルマリン、次亜塩素酸ナトリウム、イソプロパノール、フェノール、塩化ベンザルコニウム、クロルヘキシジン、塩酸アルキルジアミドエチルグリシン、グルタルアルデヒド、グルコン酸クロルヘキシジン、チアベンダゾール、2,4,5,6-テトラクロロイソフタルニトリル、ベンズイミダゾール系化合物、有機ヨウ素系化合物、有機窒素硫黄系化合物、アミノメタル銀（株式会社日鉾製）等が用いられる。

【0014】水中生物付着防止剤としては2-メチルチオ-4-1-ブチルアミノ-6-シクロプロピルアミノ-S-トリアジン、2,3,5,6-テトラクロロ-4-(マチルスルフォニル)ピリジン、アミノメタル銅（株式会社日鉾製）、塩化トリフェニルスズ、酢酸トリフェニルスズ、水酸化トリフェニルスズ、トリブチルスズオキサイド、塩化トリプロピルスズを挙げられる。

【0015】さらに、香料としては天然香料や合成香料が用いられる。その天然香料としてスベアミントオイル、ペパーミントオイル、シトロネラオイル、ユーカリオイル、カスカリラオイル、バーチオイル、シナモンオイル、クローブオイル、ニンニクオイル、ハッカオイル、マジョラムオイル、ナツメグオイル、パルマローザオイル、シソオイル、ローズオイル、セイボリオイル、ローズマリーオイル、ラベンダーオイル等から選んだ1種または2種以上を組合わせたものが用いられる。合成香料としては、酢酸アミル、α-アミルシンナミックアルデヒド、サリチル酸イソアミル、アニスアルデヒド、酢酸ベンジル、ベンジルアルコール、ボルネオール、1-カルボン、メントール、シトラール、シトロネラール、シトロネロール、クマリン、オイゲノール、サリチル酸メチル、バニリン、テルピネオール等から選んだ1種または2種以上を組合わせたものが用いられる。また、天然香料や合成香料を混合したのものも包接することが可能である。

【0016】農薬としては、殺虫剤、殺菌剤、殺線虫剤、殺ダニ剤等があげられる。殺菌剤としてはチオカーバメイト剤（マンゼブ等）、有機硫黄系剤（キャプタン等）、有機リン剤（O,O-ジイソプロピル-S-ベンジルチオホスフェート等）、有機塩素剤（ペンタクロロフェノール等）、有機ヒ素剤（メチルアルセニックジメチルカーバメイト等）、脂肪族ハロゲン剤（臭化メチ

(9)

特開平7-173452

ル等)が挙げられる。

【0017】また殺虫剤としては、有機リン殺虫剤(ジクロルボス等)やカーバメイト系殺虫剤(1-ナフチル-N-メチルカーバメイト等)、有機ハロゲン系殺虫剤(ディーディーティ等)、ニコチン類(ニコチン等)、フルオロ酢酸アミド、ピレスロイド類(ピレスリン、アレスリン等)、植物由来の精油(シネオール、ディルオイル、日本ハッカオイル、ユーカリオイル、ターペンティンオイル等)、ホウ酸等が用いられる。

【0018】殺ダニ剤としては、ケルセン、ブクロノール、クロルベジレート、クロルプロピレート、フェニソプロモレート、ラベンダーオイル、メリッサオイル、ペパーミントオイル、サルビアオイル、ローズマリーオイル等が用いられる。

【0019】殺線虫剤としては、クロルピクリン、2,3-ジクロロプロパンと1,3-ジクロロプロパンの混合物、1,2-ジプロモメタン、メチルイソシアネートがあり好ましくは、クロルピクリン、2,3-ジクロロプロパンと1,3-ジクロロプロパンの混合物等が用いられる。

【0020】

【作用】無機多孔質微粒子に抗菌性物質、水中生物付着防止剤、香料、農薬から選んだ1種または2種以上を組合わせたものを包接するとともに、高分子材料で外被することによって、水中や高温下の条件においても包接された抗菌性物質、水中生物付着防止剤、香料、農薬が溶出や揮発しにくくなる。また、その高分子材料としてはタンパク質、多糖類、合成樹脂、ラテックス、ステロイドから選んだ1種または2種以上を組合わせたものや水溶性のものによっても無機多孔質微粒子に包接された機能性物質が溶出や揮発されにくくなる。また、水溶性のものを用いる場合には、その溶解性を調整することにより水中に浸漬してから前記包接物が流出するまでの時間が調整が可能となり、水中における徐放性が実現できる。

【0021】

【実施例】以下本発明の実施例を図面を参照しながら説明するが、本発明は本実施例に何ら制約されることはない。

【0022】図1及び図2は、水中生物付着防止剤を中空部に包接してゼラチンで多孔質シリカ(商品名:ゴッドボール、鈴木油脂工業株式会社製)を外被した構造を断面説明図である。これは、前記多孔質シリカ1の中空部2に包接された水中生物付着防止剤3が微小空孔4にも充填されている状態で、外周部のみにゼラチン5を外被したものである。また、図示していないが、前記多孔質シリカ1の中空部2のみに水中生物付着防止剤3が包接され、ゼラチン5で外被されるとともに微小空孔4にもゼラチン5が充填された状態のものもある。

【0023】(実施例1)実施例1として、多孔質シリ

カ(商品名:ゴッドボール、鈴木油脂工業株式会社製)200gに水中生物付着防止剤として防藻剤2,3,5,6-テトラクロロ-4(マチルスルフォニル)ピリジン(商品名:Densil-S-100アイシアイジャパン株式会社製)の粉末20gをメチルエチルケトンの溶媒に溶かして、前記多孔質シリカに含浸させた後に、約50℃で2時間乾燥させた。このようにして得られた防藻剤入り多孔質シリカ全量をゼラチン(商品名:ゼラチン21 新田ゼラチン株式会社製)2重量%水溶液4000gに分散し、スプレードライ装置(商品名:CL-8 大川原化工機株式会社製)を使用して150℃、3000回転/分の条件下でゼラチンでコーティング処理した水中生物付着防止剤入りゼラチンを外被した多孔質シリカを得た。

【0024】(実施例2)実施例2として、揮発性の高いジャスミン香料液20gを包接した多孔質シリカ200g(商品名:ゴッドボール 鈴木油脂工業株式会社製)を、メチレンクロライドを溶媒にコレステロール:エチルセルロース:ポリエチレングリコール(分子重20000)=1:2:1の比で混合して10重量%溶液300gに分散し、それを真空凍結乾燥機(1リットル用試験機 東洋技研株式会社製)を用いてコーティング処理を行い、コレステロール、エチルセルロース、ポリエチレングリコールにより外被したジャスミンの香りがする多孔質シリカを得た。

【0025】(実施例3)実施例3として、抗菌性物質としてカワラヨモギ抽出物5gを包接した多孔質シリカ10gを、メタノールを溶媒にエチルセルロース3重量%混合した溶液125gに分散し、連続造粒乾燥機(大川原化工機株式会社製)により10分間造粒乾燥を行い、エチルセルロースで外被した抗菌性多孔質シリカを得た。

【0026】(比較例1,2,3)比較例1,2,3として、実施例1,2,3のコーティング処理を行っていないものを得た。

【0027】(実施例1及び比較例1のテスト)実施例1及び比較例1は、キシレンに溶解したアクリル樹脂系塗料に夫々5重量%になるように調整し、防藻剤入り油性アクリル樹脂系塗料を作製して、実際に船底に塗布をおこなって海中浸漬により防藻テストを行い、8週間の期間に渡って、1週間毎に藻の付着を肉眼により観察したものを表1に示した。実施例1は比較例1と比べてゼラチンによってコーティングされているので海中への溶出速度が遅くなっているため表1に示すとおり、船底の水中生物の付着を長期間に渡って防止できた。

【0028】

【表1】

【0029】(実施例2及び比較例2のテスト)実施例2及び比較例2は、アクリルエマルジョン系塗料に夫々5重量%になるように調整し、ジャスミンの香料入った

(10)

特開平7-173452

アクリルエマルジョン系塗料を作製して、厚さ0.1mm、5cm四方のベニヤ板に約3gを均一に塗布して、5時間20℃で乾燥した。そして、塗料が塗布されたベニヤ板を室内温度が30℃、湿度が90%の恒温恒湿槽にて腐食テストを行い、官能試験によりその香料の匂いなくなるまでの日数を表2に示した。本例ではコーティング処理しているために比較例2と比べて、表2に示すように、腐食テストでの持続期間は圧倒的に長かった。また、これ以上厚さのあるベニヤ板でも香料の持続期間は同じであった。

【0030】

【表2】

【0031】（実施例3及び比較例3のテスト）実施例3及び比較例3は、アクリルエマルジョン系塗料に夫々5重量%になるように調整し、抗菌剤の入ったアクリルエマルジョン系塗料を作製して、1cm四方の透明アクリル樹脂板に約2gを塗布して、室温で5時間乾燥した。その後屋外に放置して、抗菌効果を8週間の期間に渡って、1週間ごとに細菌類及び真菌類に対する評価をした。そのテストに用いられた細菌類としては、バチラスサブチリス（*Bacillus subtilis*）、スタフィロコッカス アウレウス（*Staphylococcus aureus*）、大腸菌（*Escherichia coli*）、シュードモナス アエルギノサ（*Pseudomonas aeruginosa*）、また、真菌類としては、アスペルギルス ニガー（*Aspergillus niger*）、アスペルギルス オリゼ（*Aspergillus oryzae*）、ムコール ルーキシ（*Mucor rouxi*）、サッカロマイセス セルビシエ（*Saccharomyces cerevisiae*）がある。抗菌テストは、グルコース1%（w/v）（特級グルコース 和光純薬株式会社製）、イーストエキストラクト2%（w/v）（ディフコイーストエキストラクト ディフコ社製）、ペプトン1%（w/v）（ディフコペプトン ディフコ社製）の濃度でpH6.8に調整して10ccずつ各試験管に分注してオートクレーブにより滅菌処\*

\* 理したGYP液体培地に、細菌類及び真菌類が10万個/gになるように調整して、これに、フィールドテストを行ったアクリル樹脂板を試験管内に入れ、細菌類は37℃で、真菌類は28℃で夫々恒温槽にて3日間培養して、生育状況を肉眼観察によりおこなった。実施例3はエチルセルロースでコーティングされているために必要以上には放出しないので、比較例3と比べて表3に示すとおり効果が長かった。

【0032】

【表3】

【0033】以上の結果より、コーティング処理した実施例のほうが比較例より効力が長期間に渡って持続していることが各試験の結果を表した表1、2、3により示される。

【0034】

【発明の効果】高分子材料を外被することにより、包接された抗菌性物質、水中生物付着防止剤、香料、農薬が必要以上に短時間で溶出したり揮発したりすることを防止して、長期間に渡って効果を持続することが出来る。さらに高分子材料としてはタンパク質、多糖類、合成樹脂、ラテックス、ステロイドから選んだ1種または2種以上を組合わせたものや水溶性のものを用いることにより、良好な結果が得られる。特に、水溶性のものを用いた場合には、その溶解性を調整することにより水中に浸漬してから前記包接した物が溶出するまでの時間の調整が可能となり、水中における徐放性の実現でき、船底塗料や防藻剤及び持続性の長い芳香剤としてすぐれた効果を発揮できる。

【図面の簡単な説明】

【図1】本発明の実施例の多孔質シリカの断面説明図

【符号の説明】

1. 多孔質シリカ
2. 中空部
3. 水中生物付着防止剤
4. 微小空孔
5. ゼラチン

フロントページの続き

(51)Int.Cl. <sup>°</sup>	識別記号	片内整理番号	F I	技術表示箇所
C 01 B 33/18		E		
C 05 G 3/00	1 0 3	7537-4H		
C 11 B 9/00		Z 2115-4H		